

A Simplified Weinbaum Function

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Received May 11, 1971

Energy calculations, in the two-electron approximation, are performed for LiH and Li₂ in order to illustrate the efficacy of wave functions containing a distance dependent orbital parameter in conjunction with a second variational parameter.

Harriss, Mitchell, and Musulin [1] have shown that an orbital parameter which varies with internuclear distance provides, in the two-electron Heitler-London approximation, the usual results with less calculation effort. The purpose of this investigation is to ascertain if the introduction of an additional variational parameter into a wave function containing a distance dependent orbital parameter yields the usual improvement with less than usual calculation effort.

The test parameter is the ionic parameter [2]. One covalent molecule, Li₂, and one ionic molecule, LiH, are used for test molecules. The LiH calculation is more complex in that two different variational parameters are necessary for a complete description of the ionic structures. The constants, *A* and *B*, in the expression for the orbital parameter, *z*, as a function of internuclear distance, *R*,

$$z = A \exp(-R) + B \quad (1)$$

were determined from the following models: (1) all electrons contribute to the united and separated atoms; (2) only valence electrons, in the presence of unscreened nuclei, contribute; and (3) only valence electrons, in the presence of completely screened nuclei, contribute. The derived (*A*, *B*) pairs for these models are (1.84, 2.23), (1.95, 1.30), and (0.70, 1.00), respectively, for the Li₂ calculation and (0.90, 1.92), (0.80, 1.15), and (0.70, 1.00), respectively, for the LiH calculation. The atomic wave functions used were

$$\begin{array}{ll} \frac{1}{\sqrt{\pi}} z^{(3/2)} \exp(-\varrho) & 1s \text{ Slater and Hydrogen-like} \\ \frac{1}{4\sqrt{2\pi}} z^{(3/2)} (2 - \varrho) \exp(-\varrho/2) & 2s \text{ Hydrogen-like} \\ \frac{1}{4\sqrt{6\pi}} z^{(3/2)} \varrho \exp(-\varrho/2) & 2s \text{ Slater} \end{array}$$

where $\varrho = zr$.

The values of the total energy, $-E$, at the minimum, R_e ; the dissociation energy, D_e , assuming 50.0 bohr as representing separated atoms; the change in energy, $-\Delta E$, with respect to the simple Heitler-London calculation; the values of the new variational parameters; and the quantity $[-2(\text{kinetic energy})/\text{potential}$

energy], Vir Test, are given in Table 1. (The values of ΔE were obtained after calculation errors were corrected in the programs of Harriss *et al.* [1]). The Li_2 calculation was performed with hydrogen-like wave functions while the LiH calculation was performed with nodeless Slater [3] functions. The varied selection of basis function was made to ascertain if the use of a distance dependent orbital parameter altered the validity of the nodeless functions as a good approximation for the usual hydrogen-like functions which create a slightly more complex calculation. In keeping with the framework of simplicity, the Mulliken approximation [4] was used to evaluate some of the two-centered integrals. Since the primary purpose of this investigation is to demonstrate the efficacy of the distance dependent orbital parameter, no attempt was made to use a highly refined mesh in the minimization process. Table 1 also includes the pertinent experimental values [5] and previous theoretical results [6, 7] using a simple Heitler-London ionic model.

In general, the results are similar to those reported by Harriss *et al.* [1] but with improvement in predicted energies and with additional information concerning ionic contributions. The best choice of constants in Eq. (1) is from a model resembling the model of the calculation, *viz.* a two-electron average. Although complete screening is used in the two-electron Hamiltonian, that method gives a slightly poorer predicted energy. Whether the effect is correct or whether it results from the less refined minimization is not pertinent to establishing a simplified calculation scheme.

As expected, the amount of energy improvement, ΔE , is much greater in the LiH calculation than in the Li_2 calculation. For a given molecule, the greatest improvement is with the orbital exponent model yielding the poorest simple Heitler-London energy value which is the usual result in a two-parameter variation. Incrementation by 0.1 was not sufficient to detect the small change in E in the Li_2 calculation using model (3) for the orbital exponent. In every case the value of D_e is increased since the atomic values are not altered by the introduction of the new variational parameter.

The best model choice yields a good but overestimated value of R_e ; improvement of the model by including inner shell electrons would shift R_e toward the nucleus [8]. A more refined minimization would yield better wave functions which would satisfy the quantum mechanical Virial Theorem [9]. The coefficients given in Table 1 correctly show the preponderance of the $\text{Li}^+ \text{H}^-$ structure in the calculation with the best model choice.

In summary, the present investigation verifies the utility of a distance dependent orbital exponent in simple theoretical calculations. Essentially this technique saves the time and cost of one variable minimization without a great loss in accuracy in R_e and E values. Further, a reasonably good wave function, consistent with the simplicity of calculation, is obtained. The techniques demonstrated in this paper should provide workers in non-theoretical fields a simple tool for estimating atomic and molecular energies. These techniques will also be useful for workers with limited computing facilities. Theoretical workers as well as those with more extensive computing facilities may wish to use the rigorous, sophisticated techniques which have been applied to Li_2 and LiH [10].

Table 1. Summary of results

Compound	Function	Orbital Parameter	$R_e(\text{h.})$	$-E(\text{h.})$	$D_e(\text{h.})$	$-\Delta E(\text{h.})$	Vir Test	Ionic ($A^- B^+$)	Parameters ($A^+ B^-$)
Li ₂	Hydrogen-like	Six electron average	3.00	0.0784	0.2066	0.0573	0.80	0.6	0.6
		Two electron average	5.50	0.2787	0.0512	0.0031	0.82	0.2	0.2
	Slater ^b Experimental ^a	Two electron average with screening	8.00	0.2733	0.0233	0.0000	0.86	0.0	0.0
		Fixed by Slater's rules	4.54	0.166	0.0419	0.0018	—	—	—
LiH	Slater	Four electron average	2.10	0.4416	0.5058	0.4026	0.78	1.0	0.2
		Two electron average	3.05	0.7418	0.1860	0.1026	0.86	0.5	0.7
	Slater ^c	Two electron average with screening	2.70	0.7405	0.1572	0.0887	0.99	0.4	2.0
		Minimized, distance independent	2.73	0.8370	0.0802	0.0208	—	—	—
	Hydrogen-like ^c Experimental ^a	Minimized, distance independent	2.35	0.7813	0.1488	0.0836	—	—	—
		Experimental ^a	3.01	0.7897	0.095	—	1.00	—	—

^a Ref. [5]. — ^b Ref. [6]. — ^c Ref. [7].

Acknowledgements. The authors gratefully acknowledge the *gratis* use of computing equipment of the Data Processing and Computing Center of Southern Illinois University. Thanks is accorded to the Graduate School of Southern Illinois University for a fellowship for one of us (CMW). One of us (BM) acknowledges the assistance of Professor K. A. Van Lente in directing this project during a sabbatical leave.

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